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Feasibility of using non-vegetated baffled submerged constructed wetland system for removal of heavy metals, COD and nutrients from hyper-saline hazardous landfill leachate

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ABSTRACT

Hazardous landfill generates severe leachate containing salts, heavy metals and toxic refractory compounds which adversely affect human health and environment. Constructed wetland (CW) systems are robust and applicable for removal of organics and nutrients from sanitary landfill leachate. However, its effectiveness for the treatment of hyper-saline hazardous landfill leachate (HHLL) remains unexplored. The feasibility of using non-vegetated baffled submerged constructed wetland (BSCW) system for the treatment of HHLL at different hydraulic retention times (HRTs) was investigated. The results revealed that the removal efficiency of CODt and nitrification efficiency was significantly increased from 17.4 ± 2.7% to 46.5 ± 2.9% and from 35.6 ± 2% to 65.4 ± 3.2% at increasing the HRT from 1.7 to 10 days respectively. However, the major portion of CODt in the treated effluent was mainly in a soluble form which accounted for 90% of CODt. Moreover, the module achieved removal efficiency of 95.9 ± 3.6% for Fe^{3+}, 95.1 ± 2.9% for Zn^{2+}, 93 ± 3.9% for Cu^{2+}, and 92.4 ± 3% for Mn^{2+} at an HRT of 10 d.

Keywords: Constructed wetland; Hyper-saline hazardous landfill leachate; Nitrification; Salinity; HRT; Toxicity; Heavy metals

1. Introduction

Alexandria is the 2nd largest city in Egypt and hosts more than 1900 industrial facilities, including chemicals, petrochemicals, food processing, textile, construction, pharmaceuticals, textile, cement, electronics, and paper mill [1–7]. Huge quantities of hazardous industrial solid waste are daily generated and mainly dumped into local landfill creating serious environmental problems. Landfilling is still one of the most appropriate technologies for the final disposal of hazardous solid waste due to its economic advantages [8,9]. However, a considerable amount of hazardous leachate is produced due to the decomposition of solid wastes which affect negatively on the ground water and vegetation of surrounding areas [10]. The hazardous landfill leachate is mainly hyper-saline and highly contaminated with heavy metals and toxic compounds [10]. Therefore, treatment of hyper-saline hazardous landfill leachate (HHLL) is crucial and necessary [11,12]. Advanced oxidation processes [4,11–17] and physico-chemical treatment technologies such as ozonation, coagulation/flocculation, ultra filtration, ion exchange and reverse osmosis is effective for treatment of HHLL [18]. However, these technologies require high skills for operation and maintenance which are not available in low income countries. Moreover, treatment of HHLL using conventional biological treatment processes are not recommended due to the presence of refractory toxic compounds and heavy metals [19]. Alternatively, constructed wetland (CW) systems are considered the most economic and effective treatment technology particularly for developing

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countries, due to their minimal cost for operation and maintenance [20]. Moreover, CW systems are widely used for the treatment of saline wastewater [21], metallurgic wastewater [22] and have been reported to be efficient for the treatment of sanitary landfill leachate containing recalcitrant and inhibitory compounds [23–25]. Fortunately, sulfate reducing bacteria (SRB) situated in the anaerobic zone of CW play a key indirect role for removal of heavy metals. Sulfide resulted from dissimilatory sulfate reduction [Eq. (1)] would remove heavy metals (M) from wastewater via precipitation of metal sulfide [Eq. (2)] [26]. SRB utilizes one mole of sulfate to produce one mole of sulfide which increased the alkalinity and raised the pH value of CWs based on Eq. (1). Fe^{3+}, Zn^{2+}, Cu^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} and Mn^{2+} can be easily precipitated as metal sulfides in CW systems [27,28]. However, high sulfide concentrations negatively affected on the nitrification process where nitrifiers have to compete with the rapid chemical oxidation of sulfide with oxygen.

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2O + 2CO_2 \qquad (1)$$

$$S^{2-} + M^{2+} \rightarrow MS \qquad (2)$$

A number of previous studies were conducted to evaluate the tolerance ability of vegetated CW to high contaminant levels of ammonia, salts and heavy metals. Surrency [29] found that ammonia concentration exceeded 160–170 mg/L adversely affected on *T. latifoliawas*, while *S. validus* tolerated the extreme conditions. *Scirpus acutus* was negatively affected at ammonia concentration varied from 20.5 to 82.4 mg/L [30]. Likewise, COD level exceeded 200 mg/L would disrupt the metabolism of *P. australisto* [31]. Meky et al. [32] found that the vegetated CW system treating HHLL was not efficient and the plants died after an operational period of 75 d. Thus, such assessments are not only useful for the understanding of the tolerance of wetland plants but also provide the opportunity to select the most appropriate CW system for treatment of highly contaminated HHLL. A novel non-vegetated baffled submerged constructed wetland (BSCW) was designed and extensively investigated here for treatment of HHLL. Baffled flow mode and hybrid packing media were successfully combined in one module to overcome the limitations of conventional CW systems. The baffles would increase the length of water path, oxygen transfer from the air. The hybrid media (sand and gravel) would provide filtration/adsorption and formation of several bacterial consortium to grow and efficiently eliminate all contaminants. However, the efficiency of BSCW for treatment of HHLL is hydraulic retention time (HRT) dependent. Muñoz et al. [34] found that the COD and nitrogen removal efficiencies were substantially improved by increasing the HRT from 3 to 7 d. An appropriate microbial bacterium community could be established in CW system and have adequate contact time to remove contaminants at long HRT [35,36]. Huang et al. [37] found that ammonia and total nitrogen (TN) concentrations in the treated effluent of CW system significantly dropped at increasing HRT. Similar trends were observed by Toet et al. [38] 0.3, 0.8, 2.3, and 9.3 days where nitrogen removal in CW system was increased by increasing the residence time from 0.3 to 0.8 d. Lee et al. [39] reported that long HRT is required for nitrogen removal as compared to elimination of organics.

The present study aims to explore the feasibility of using non-vegetated baffled submerged constructed wetland (BSCW) system for the treatment of hyper-saline hazardous landfill leachate (HHLL) with emphasis on the effect of HRT on the removal efficiency of COD fractions (CODt, CODs, and CODp), heavy metals and salinity as well as nitrification efficiency. Moreover, the fate of heavy metals in the sediment and the effect of salinity on the COD removal and nitrification efficiency were assessed.

2. Materials and methods

2.1. Hyper-saline hazardous landfill leachate (HHLL) characteristics

The leachate used in this study was obtained from Al-Nasreya hazardous landfill site located in new Borg El-Arab city, 35 km south-west of Alexandria, Egypt. The landfill was built in 2004 for the final disposal of industrial hazardous solid waste such as asbestos, ash from heavy fuel oils, contaminated soil, heavy metals, sludge from galvanic processes, insoluble metal salts, inks, dyes, lacquers, paint sludge, resins, polymers, and chemical containers [1]. The landfill produces approximately 10 m^3/d leachate which evaporated in a natural solar pond creating serious environmental problems. The HHLL was daily collected and fed to the non-vegetated baffled submerged constructed wetland (BSCW) system for a period of 250 d. The main physicochemical characteristics of HHLL are summarized in Table 1. The biodegradability of HHLL was quite low as BOD_5/COD ratio was only 0.2 ± 0.1. Moreover, HHLL was very toxic where EC50 was equivalent to 2.5 and salinity highly fluctuated from 40, 400 to 59,700 mg/L.

2.2. Non-vegetated baffled submerged constructed wetland (BSCW) system

A schematic diagram of BSCW system at a pilot scale is shown in Fig. 1. The system consisted of three surface flow rectangular consecutive units. The flow mode was horizontal in the 1st unit and vertical in the 2nd and 3rd unit respectively. The module was manufactured from polyvinyl chloride (PVC). The dimensions of each unit were 50 cm length, 30 cm width and 40 cm depth with working volume of 53 L. Each unit was filled with 10 cm of sand (1–8 mm) at the top and 17 cm of coarse gravel (1–4 cm) in the bottom. The BSCW system was operated at an ambient temperature of 17–32°C. The HHLL was continuously fed to the module using aperistaltic pump (Masterflex – USA, Cole-Parmer Instrument Company). The BSCW units were placed at different water head levels to provide a natural flow under gravity. The module was initially operated for acclimatization period of 30 d of which the COD in the treated effluent was daily analyzed. The COD removal efficiency was largely fluctuated at 1–10 d and remained at a level of 43 ± 2.5%–48 ± 2.7% at day 15 which indicates the module attained the steady state operating conditions. The BSCW system was continuously operated for a period of 252 d at different flow rates of 16, 19, 24, 32, 48 and 94 L/d and HRTs of 10, 8.3, 6.6, 5, 3.3 and 1.7 d. The acclimatization period of 15 d was considered after changing the HRT in each operation phase.

Table 1
Hypersaline hazardous landfill leachate (HHLL) characteristics

Parameters	Min.	Max.	Average ± SD
pH	7.92	8.34	8.16 ± 0.14
CODt, mg/L	3690	5430	4814.69 ± 323.48
CODs, mg/L	3560	4995	4298.09 ± 332.71
CODp, mg/L	60	1190	516.59 ± 281.52
BOD_5, mg/L	850	1100	953.69 ± 93.02
BOD_5/COD	0.18	0.23	0.2 ± 0.02
TN, mg/L	305.82	459.63	374.26 ± 29.54
TKN, mg/L	305	457.52	372.82 ± 29.47
NH_4^+-N, mg/L	102	235.28	151.58 ± 29.46
$N_{organic}$, mg/L	142	306	221.24 ± 36.14
NO_3^--N, mg/L	0.7	2.61	1.48 ± 0.49
Salinity, mg/L	40400	59700	49823.24 ± 4908.17
TSS, mg/L	912	1480	1046.35 ± 95.34
VSS, mg/L	85	300	208.07 ± 50.25
VSS/TSS	0.09	0.28	0.2 ± 0.05
Cu^{2+}, mg/L	33.8	40.56	37.58 ± 2.35
Mn^{2+}, mg/L	20.08	27.52	23.67 ± 2.97
Fe^{3+}, mg/L	19.97	22.84	21.28 ± 0.96
Zn^{2+}, mg/L	39.18	40.24	40.02 ± 0.42
Ni^{2+}, mg/L	31.94	41.43	36.29 ± 3.67
Pb^{2+}, mg/L	0.16	0.54	0.3 ± 0.17
Cr^{3+}, mg/L	0.94	2.13	1.53 ± 0.44
Cd^{2+}, mg/L	0.14	0.45	0.35 ± 0.11

2.3. Analytical methods and calculations

The influent and effluent samples were collected three times per week and analyzed for pH, total chemical oxygen demand (CODt), salinity, total suspended solids (TSS), volatile suspended solids (VSS), biochemical oxygen demand (BOD_5), sulfate (SO_4^{2-}), sulfide (H_2S), total Kjeldahl nitrogen (TKN), ammonium-nitrogen (NH_4^+-N) and nitrate (NO_3^--N) according to APHA [40]. A portion of the samples was filtered through 0.45-µm Millipore membrane filter paper (Whatman, UK) for the determination of soluble chemical oxygen demand (CODs). Particulate chemical oxygen demand (CODp) was calculated from the difference between CODt and CODs concentrations. The toxicity of HHLL and treated effluent was measured using Microtox analyzer 500. Heavy metals of water and sediment samples were analyzed using atomic absorption spectrophotometer (Shimadzu, Model AA7000). 2.0 g sediment samples were collected from the packing media for analysis of heavy metals. The samples were initially dried in the oven at a temperature of 105°C for 24 h. Heavy metals were extracted using 3 ml HNO_3 and 9 ml HCl and further digested for 3 h at a temperature of 105°C.

The organic nitrogen ($N_{organic}$), total in organic nitrogen (TIN), and total nitrogen (TN) were calculated based on the following equations:

$$N_{organic} = TKN - NH_4^+\text{-N} \quad (3)$$

$$TIN = NH_4^+\text{-N} + NO_2^-\text{-N} + NO_3^-\text{-N} \quad (4)$$

$$TN = N_{organic} + TIN \quad (5)$$

2.4. Mathematical model

The modified plane equation was used to assess the combined effect of HRT and salinity concentrations on the COD removal and nitrification efficiency

$$\text{Removal } \% = y + ax + by \quad (6)$$

where y is constant, x is the salinity concentrations (mg/L), y is the operational HRT (days) of BSCW system, a and b are the coefficients.

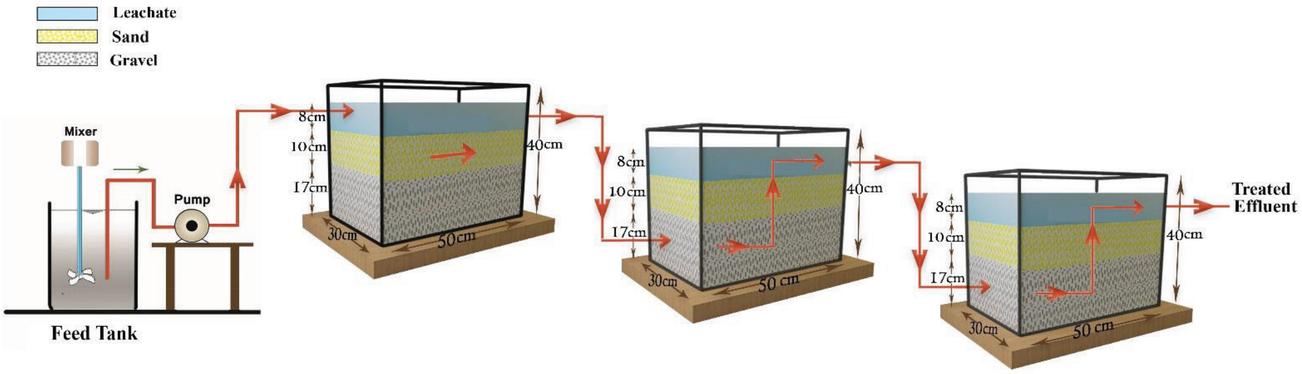

Fig. 1. Schematic diagram of the pilot scale of non-vegetated baffled submerged constructed wetland system treating HHLL.

Statistical regression analysis of the experimental results was assessed at two independent variables: influent salinity concentrations (*x*) operational HRT (*y*) [Eq. (6)]. The fitness of this model was further evaluated using analysis of variance (ANOVA). The significance (p-value) was considered according to a 95% confidence level. The statistical analysis and the response surface plots were carried out using Sigma Plot 10.0 software.

3. Results and discussion

3.1. Removal efficiency of COD fractions

Figs. 2a and b show the effect of HRT on the removal efficiency of CODt and CODs. The results revealed that the efficiency of non-vegetated BSCW system was gradually decreased with reducing the HRT from 10 to 1.7 d. CODt removal efficiency was significantly decreased from 46.5 ± 2.9% to 17.4 ± 2.7% at reducing the HRT from 10 to 1.7 d respectively. This is mainly due to a short contact time between the substrate and consortium bacteria responsible for bio degradation of organics. The toxicity (EC_{50}) was significantly reduced from 2.5 to 1.25 which accounted for 50% at an HRT of 10 d. However, CODt removal efficiency was slightly decreased from 46.5 ± 2.9% to 39.3 ± 2.2% at decreasing the HRT from 10 to 8.3 d respectively. Physical (filtration/adsorption) followed by bio degradation process using different consortium bacterium accumulated inside the different zones of the non-vegetated BSCW system is mainly the possible removal mechanism of CODt. Moreover, the presence of sulfate in HHLL would effectively contribute to the reduction of COD by SRB and to the precipitation of metal sulfides [24,41]. Nevertheless, these results are lower than those obtained by Comino et al. [42] where hybrid CW system achieved COD removal efficiency of 73%. The residual COD value of only 82 mg/L remained in the treated effluent of hybrid CW at a hydraulic loading rate of 5.5 cm/d [43]. Calheiros et al. [44] reported a removal percentage of 41–73% for COD in a pilot CW unit treating tannery wastewater. Herrera-Cárdenas et al. [45] found that the removal of organics was increased by increasing the HRT from 1 to 5 d. The major portion of COD in the treated effluent of BSCW system at an HRT of 10 d was mainly in the soluble form and accounted for 90% of the total COD effluent as shown in Fig. 2b. However, the removal efficiency of CODs was increased from 20.9 ± 1.1% to 31.9 ± 4.6% at increasing the HRT from 3.3 to 6.6 d, respectively. The lowest CODs removal efficiency of 16.25 ± 1.44% occurred at an HRT of 1.7 d. Apparently, the presence of salts in HHLL caused a decrease of the solubility of non-polar and weakly organics which inhibited the bio degradation of COD in a soluble form.

Three-dimensional regression analysis based on Eq. (6) was used to assess the combined effect of salinity (*x*) and HRT (*y*) on the removal efficiency of CODt and CODs. Eqs. (7) and (8) were statistically fitted to the experimental data with R^2 values exceeding 0.9. Furthermore, the effect of salinity and HRT on the removal efficiency of CODt and CODs were significant at a level of $p < 0.05$. The results revealed that salinity exceeded 48,000 mg/L adversely affected on the CODt and CODs removal as shown in Figs. 2c and d. However, increasing the HRT from 1.7 to 10 days mitigate the negative impact of salinity. Calheiros et al. [44] found that pilot CW unit treating tannery wastewater containing high salts achieved removal percentage of 41–73% for COD. A great potential for removing COD (61.5–70.5%) in CW system at the influent salt content of 2.0% was obtained by Gao et al. [46]. Nevertheless, Qiu et al. [47] reported that the COD removal efficiency significantly decreased in CW system at mixing ratio of 30% of seawater and 40% of domestic wastewater.

$$\text{CODt removal \%} = 20.5324 - 0.0002x + 3.5558y \qquad (7)$$

$$\text{CODs removal \%} = 9.3574 - 0.0045x + 3.4805y \qquad (8)$$

The CODp exhibited similar trends to CODt and CODs, except at 8.3 d HRT where the removal efficiency slightly increased from 53.6 ± 19.6% to 54.2 ± 27.5% at decreasing the HRT from 10 to 8.3 d, respectively. The CODp removal efficiencies were significantly ($p < 0.001$) dropped from 49.1 ± 30.6% to 24.2 ± 15.9% at decreasing the HRT from 6.6 to 1.7 d respectively.

3.2. Nitrogen species removal

Figs. 3a, b,c, and d show the effect of HRT on removal efficiency of the nitrogen species. The results revealed that TN, TKN, and organic nitrogen ($N_{organic}$) removal efficiencies increased by values of 11%, 11.1% and 5.6% at increasing the HRT from 6.6 to 10 d, respectively. These results are similar to those obtained by Vera et al. [48] where TN and NH_4^+-N removal efficiency increased by 10% at increasing the HRT from 3.5 to 7 d respectively. The TN, TKN and $N_{organic}$ removal efficiencies slightly decreased from 34.4 ± 3.3% to 26.1 ± 3.7 %, from 34.9 ± .4% to 26.5 ± 3.7% and from 25.5 ± 3.5% to 16.8 ± 6.5% at reducing the HRT from 5 to 3.3 d, respectively. However, the TN, TKN and $N_{organic}$ removal efficiency substantially dropped to 20.8 ± 3.25%, 21 ± 3.3% and 11.5 ± 5.7% at an HRT of 1.7 d, as shown in Figs. 3a, b,and c. $N_{organic}$ removal was mainly due to bacterial growth and ammonification (mineralization) in the anaerobic zone of non-vegetated BSCW system. Comino et al. [49] observed an increase of NH_4^+-N concentration in the effluent of hybrid CW treating cheese wastewater due to the conversion of $N_{organic}$ into ammonia. However, 133 ± 21.1, 131 ± 16.5, 163 ± 22.9, 168 ± 29.9, 170 ± 24.1 and 207 ± 21.5 mg/L of $N_{organic}$ remained in the treated effluent of BSCW at HRTs of 10, 8.3, 6.6, 5, 3.3 and 1.7 d respectively. This can be attributed to a high $N_{organic}$/TN ratio of the influent HHLL. The highest removal efficiency of ammonia was 65.4 ± 3.2% at an HRT of 10 d, which was dropped to 35.6 ± 2.0% at an HRT of 1.7 d(Fig. 3d). This was mainly due to in significant nitrification resulted from in sufficient available oxygen and residence time of nitrifiers was quite short for ammonia oxidation at an HRT of 1.7 d. This was not the case at HRT of 10 d where a considerable amount of ammonia was oxidized in the BSCW system due to sufficient contact time between the substrate and nitrifiers. These results are higher than those obtained by Gorra et al. [50] who found that the overall of ammonia removal was 26.9% in a hybrid CW treating cheese wastewater. However, both gravel and soil beds of CW systems provided similar removal efficiency of 50%

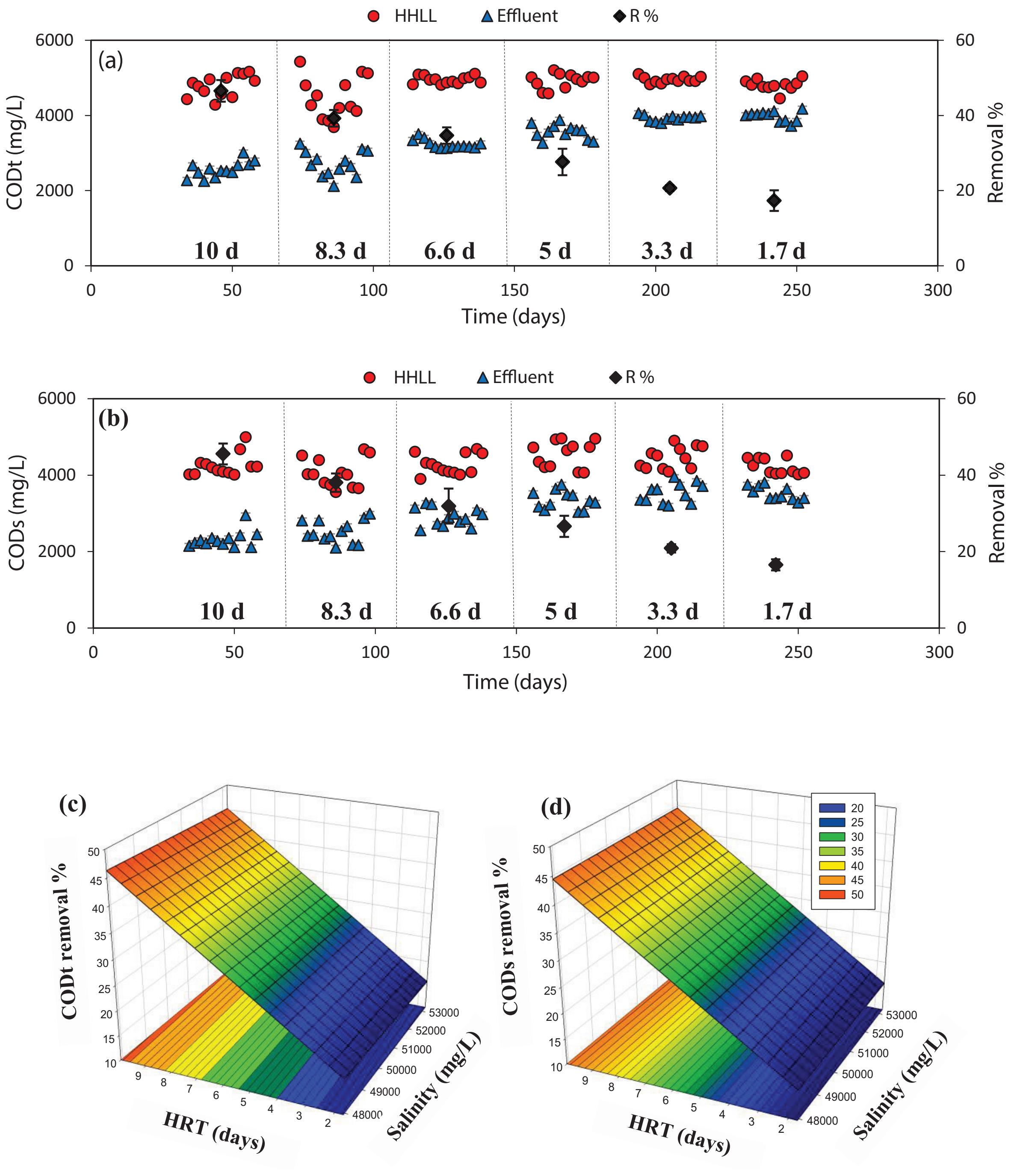

Fig. 2. Removal efficiencies of CODt (a) and CODs (b) at different HRTs and three-dimensional and contour plots of the combined effect of salinity and HRT on the CODt (c) and CODs (d).

for ammonia [51]. The results showed that only 30% of ammonia was oxidized due to nitrification at an HRT of 10 d. This indicates that portions of ammonia were removed due to volatilization, cation exchange [52] and synthesis of biomass. Total inorganic nitrogen (TIN) presumed to be highly removed in the upper layer of the non-vegetated BSCW system where available oxygen is presented creating favorable conditions for nitrifiers [51]. However, the nitrate (NO_3^--N) concentrations were quite low in the treated effluent i.e. 2.6 ± 0.8, 2.2 ± 0.8, 1.8 ± 0.6, 3.3 ± 1, 2.6 ± 1 and 2.3 ± 0.9 mg/L at HRTs of 10, 8.3, 6, 5, 3.3 and 1.7 d, respectively. This is probably due to denitrification process which occurred in the deepest layers of the BSCW system where the high porosity gravel beds might let more denitrifying bacteria to grow in the substratum. Moreover, autotrophic denitrification process could be occurred due to sulfide oxidation process coupled with the reduction of nitrate as in Eq. (9)

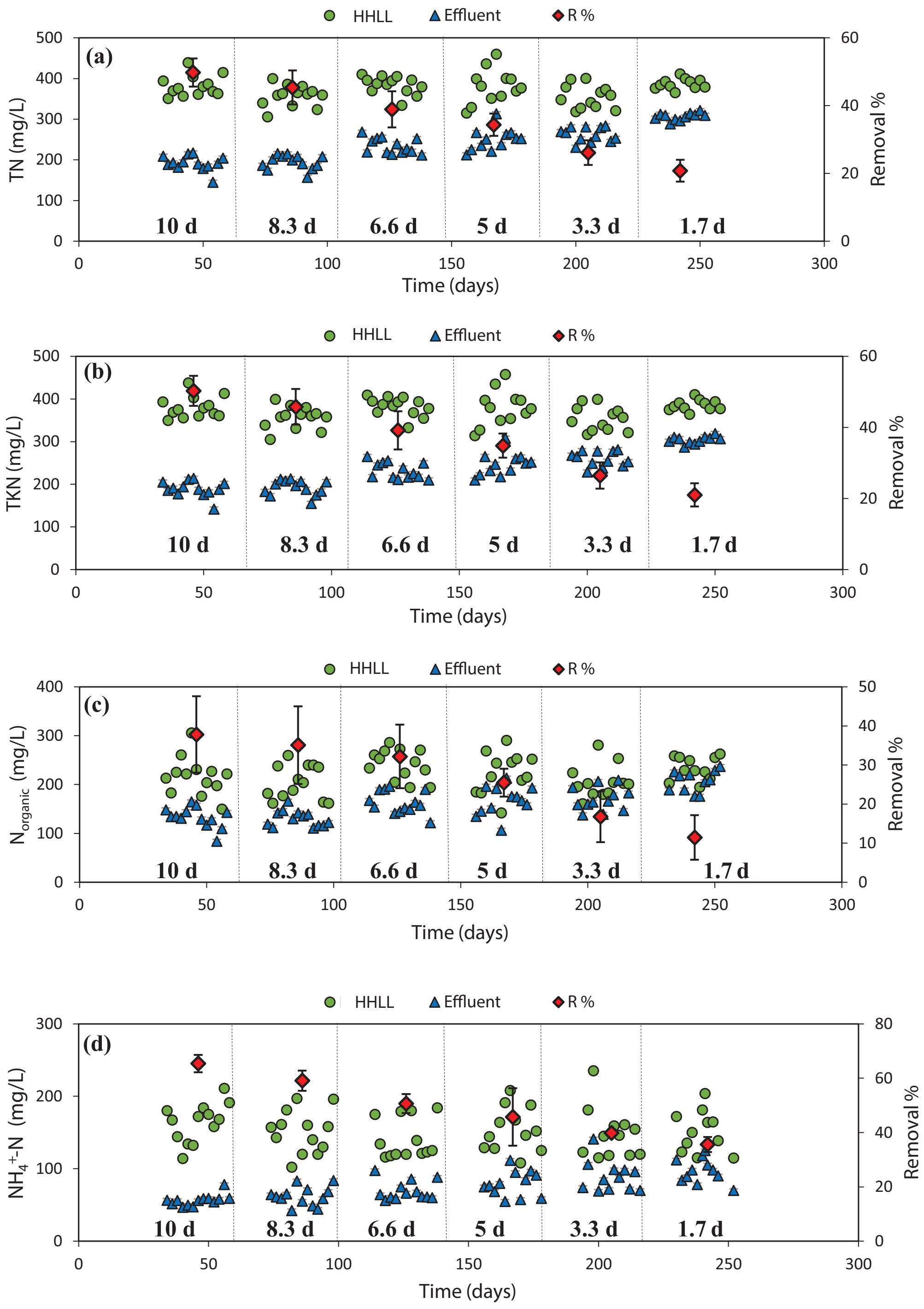

Fig. 3. Removal efficiencies of nitrogen species TN (a) TKN (b) Norganic (c) and NH_4^+-N (d) at different HRTs.

$$5HS^- + 8NO_3^- + 3H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O \qquad (9)$$

Brix [52] found that NO_3^--N was mainly removed through the denitrification process in non-vegetated CW systems where the oxygen in the substratum was absent. The NO_3^--N accumulation in vegetated CW system was quite high as compared to the non-vegetated one [51] due to release of nutrients back into the water phase.

The combined effect of salinity (x) and HRT (y) on the TN, TKN, and NH_4^+-N are presented in Figs 4a, b, and c. The predicted removal efficiencies of TN, TKN and NH_4^+-N were statistically compared to the observed data using ANOVA (analysis of variance). The results showed that the three models Eqs. (10)–(12) were quite fitted to the experimental data with R^2 values greater than 0.9. Moreover, the combined effects of salinity and HRT were significant at a level of $p < 0.05$. The nitrification efficiency and TN removal were deteriorated by increasing the salinity as shown in Figs. 4a, b, and c. However, ammonia removal remained at a high level at an HRT of 10 days which indicates that the nitrifiers could be able to grow even under the salt stress conditions. These results are consistent with the study by Corsino et al. [53] who found that high salinity did not affect nitrogen removal, where the removal efficiency reached up to 98% at salinity concentration of 50 mg/L. Nevertheless, Wu [54] reported that NH_4^+-N and TIN removal efficiency dropped from 98% to 83% and from 78% to 56% at increasing the salinity from zero to 30 mg/L for CW system treating municipal wastewater.

$$\text{TN removal \%} = 7.7217 - 0.0001x + 3.5908y \tag{10}$$

$$\text{TKN removal \%} = 5.5541 - 0.0002x + 3.6225y \tag{11}$$

$$NH_4^+\text{-N removal \%} = 31.9235 - 7.41x + 3.6355y \tag{12}$$

3.3. Coarse suspended solids and salinity removal efficiency

Figs. 5a and b show the removal efficiency of total suspended solids (TSS) and volatile suspended solids (VSS) at different HRTs. TSS and VSS removal efficiency increased from 35.6 ± 3.9% to 45.8 ± 2.7%and from 67.3 ± 5.4% to 78.5 ± 5.1% at increasing the HRT from 6.6 to 10 d. Lower TSS removal efficiency of 59.5% was recorded by Comino et al. [42] due to partial clogging of the hybrid CW. However, a considerable higher TSS removal of 96.9% and 99% was obtained by Merlin et al. [55]. The TSS and VSS removal efficiency was further decreased to 29.1 ± 1.2% & 23.9 ± 2.8% and 51.9 ± 3.7% & 43.3 ± 2.9% at reducing the HRT from 5 to 3.3 d. TSS and VSS removal efficiency was quite low at an HRT of 1.7 d as shown in Figs. 5a and b. The physical adsorption of the particles to the gravel and sand beds as well as filtration and sedimentation is probably the major removal mechanism of coarse suspended solids. However, it is likely that the clogging of the attached pores of gravel and sand beds occurred at short HRT of 1.7 d. Fig. 5c shows

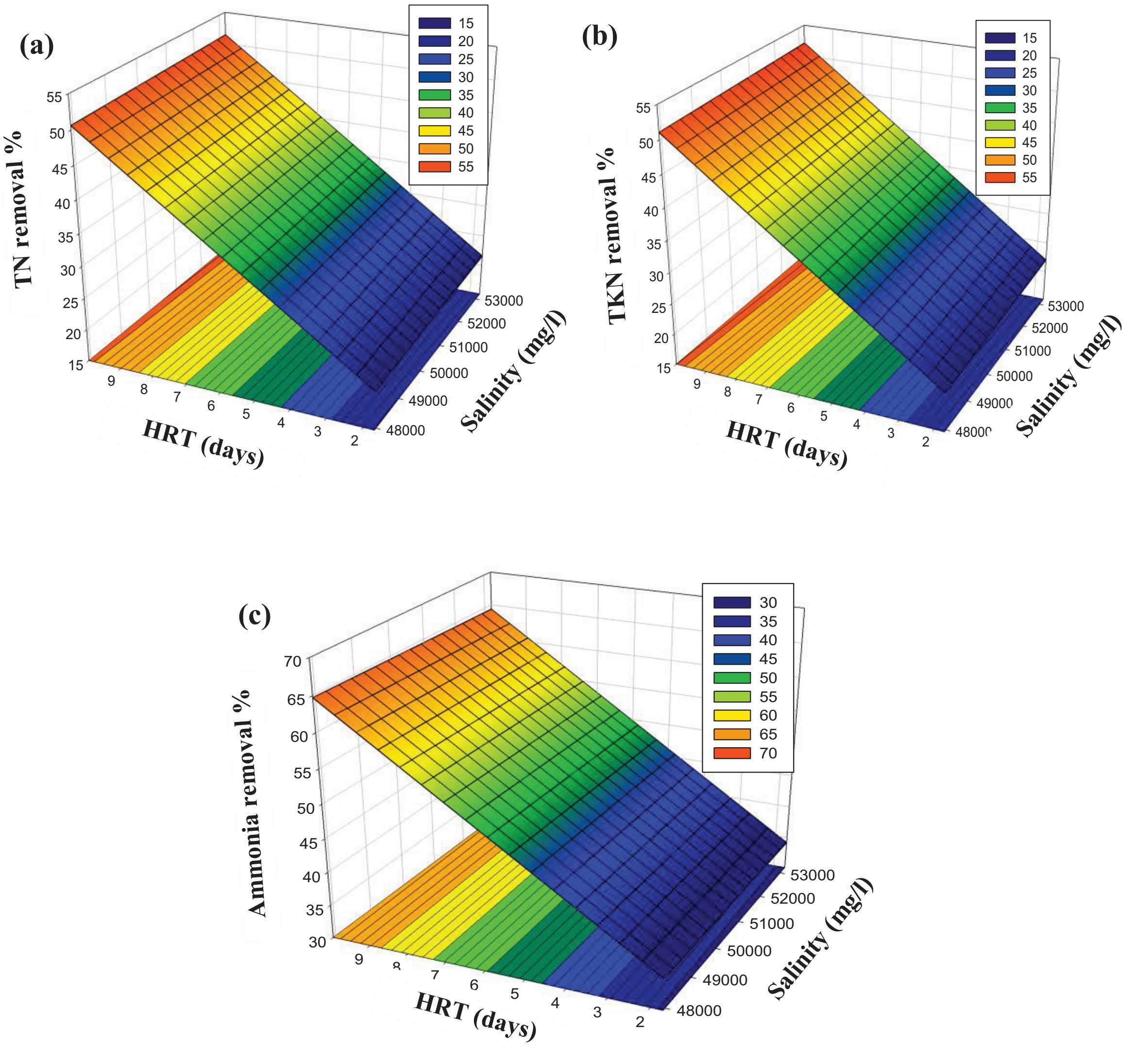

Fig. 4. Three-dimensional and contour plots of the combined effect of salinity and HRT on the TN (a) TKN) (b) and NH_4^+-N (c).

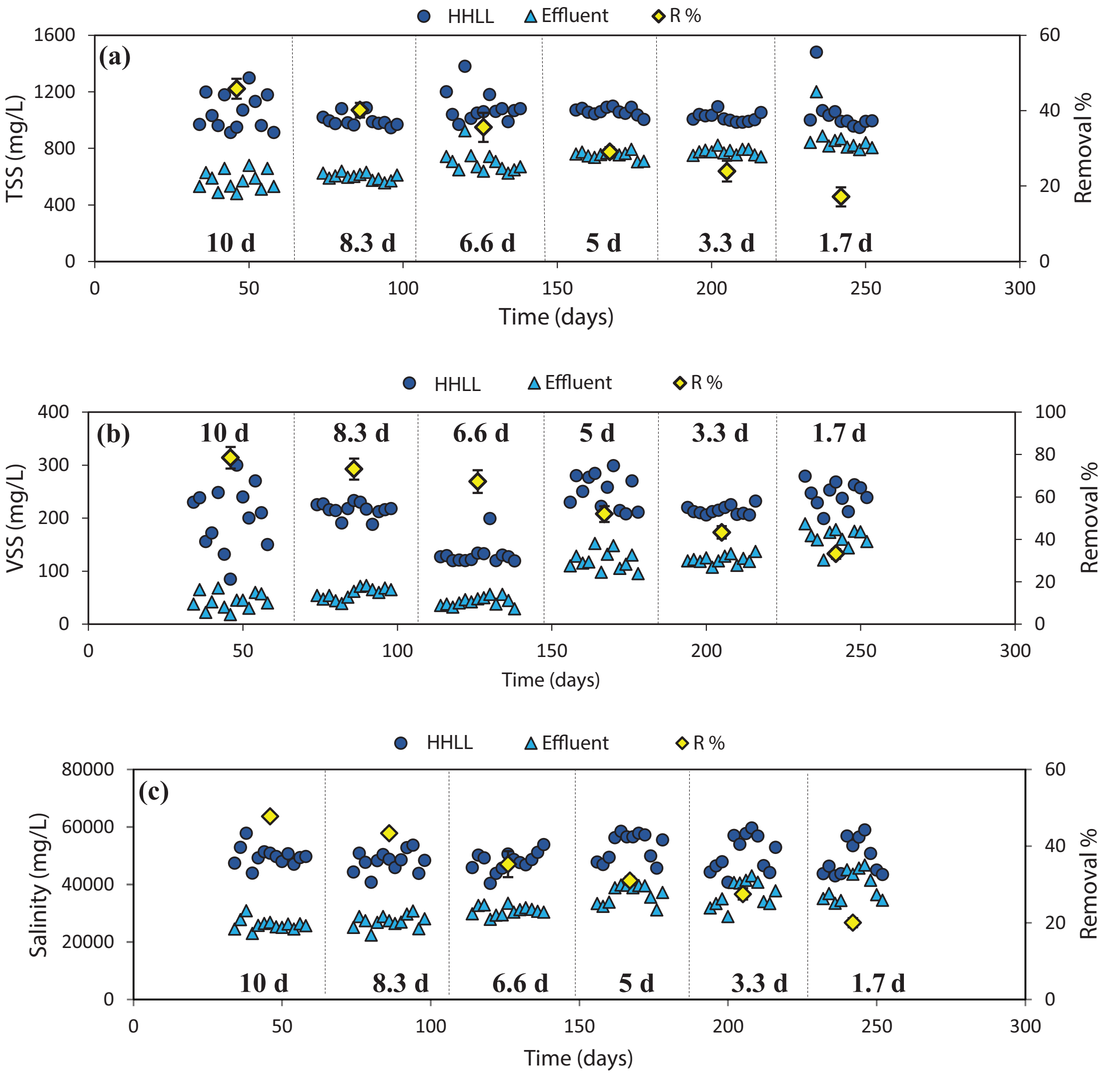

Fig. 5. Removal efficiencies of (a) TSS (b) VSS and (c) salinity at different HRTs.

the effect of HRT on salinity removal efficiency. Salinity removal efficiency amounted to 47.8 ± 0.7% at an HRT of 10 d and dropped up to 43.4 ± 0.9%, 35.3 ± 3.4%, 31.02 ± 1.1%, 27.5 ± 1.5% and 20.1 ± 1.2% at HRTs of 8.3, 6.6, 5, 3.3 and 1.7 d, respectively. However, the salinity in the treated effluent remained at a high level of 20 g/L which needs further treatment.

3.4. Fate of heavy metals

Figs. 6a, b, c, d, and 7a show the removal efficiency of heavy metals in BSCW at different HRTs. The results revealed that the system was very efficient for removal of Cu^{2+}, Mn^{2+}, Fe^{3+}, Zn^{2+}, and Ni^{2+}. However, the removal of heavy metals was HRT dependent. Fe^{3+}, Zn^{2+}, Cu^{2+} and Mn^{2+} removal efficiency significantly decreased from 90.1 ± 1.5% to 55.0 ± 1.9%, from 85.5 ± 1.5% to 44.4 ± 2.5%, from 81.4 ± 2.5% to 41 ± 2.6% and from 85.6 ± 1.6% to 14.4 ± 3.5% at reducing the HRT from 8.3 to 1.7 d respectively. 94.5% and 93.5% of Fe^{3+} was removed in passive CW treating landfill leachate [56]. A removal percentage of 86% for Cr^{3+} and 67% for Ni^{2+} were reported by Maine et al. [22] in CW system treating saline wastewater from metallurgic industries. The BSCW system removed 95.9 ± 3.6% for Fe^{3+}, 95.1 ± 2.9% for Zn^{2+}, 92.9 ± 3.9% for Cu^{2+} and 92.4 ± 3.02% for Mn^{2+} at an HRT of 10 d. This can be attributed to a combination of filtration, adsorption, biologically mediated formation of metal sulfides and subsequent precipitation processes [20,57]. The anaerobic condition prevailed in the bottom layers of packing media in non-vegetated BSCW was presumably enhanced the activity of SRB, which reduced the sulfur compounds (48 mg SO_4/L) present in HHLL to sulfide (38 mg/L).The production of sulfide caused an increase in the pH value from 8.16 ± 0.14 to 9.1 ± 0.16 due to the consumption of proton in the sulfate ions. The increase of pH value could further reduce the solubility of heavy metals and the toxicity of HHLL [58]. In addition, the toxicity of the produced metal sulfide is recognized to be relatively

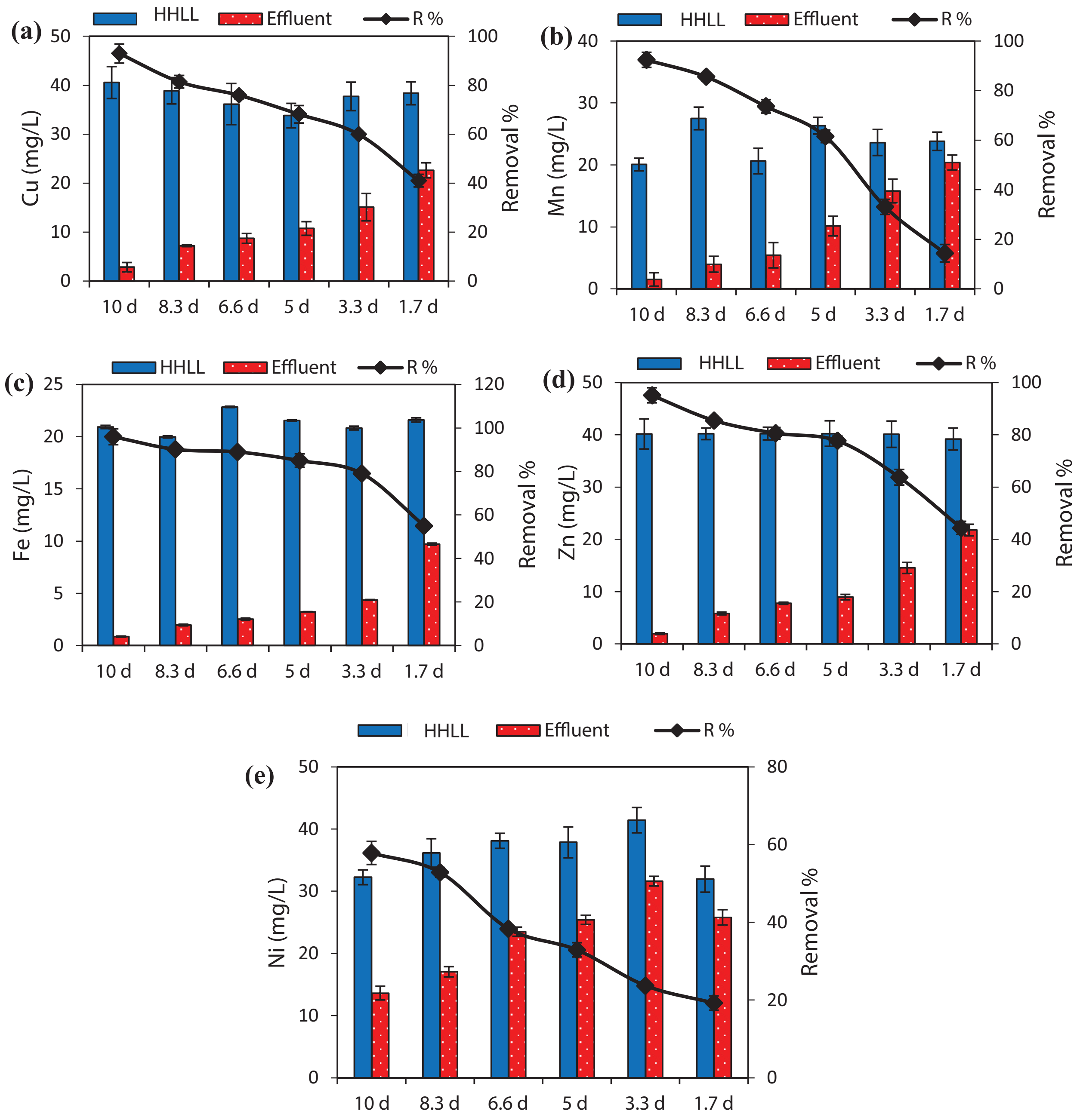

Fig. 6. Removal efficiencies of Cu^{+2} (a) Mn^{+2} (b) Fe^{+3} (c) Zn^{+2} (d) and Ni^{+2} (e) at different HRTs.

low as compared to those for the free heavy metals [59]. The sulfide was likely to react with the dissolved forms of heavy metals forming thermodynamically stable metal sulfide complexes which could be precipitated on gravel and sand beds (when the concentration exceeds the solubility limit), as described elsewhere by Meky et al. [32]. These assumptions were confirmed by the results in Fig. 7b where the major portion of metals was retained in the anaerobic zone of the packing materials. The highest accumulation rates in the sediment was for Cu^{2+} (522 ± 17 mg/kg) followed by Fe^{3+} (387 ± 21 mg/kg), Ni^{2+} (345 ± 15 mg/kg), Zn^{2+} (345 ± 15 mg/kg) and Mn^{2+} (251 ± 9 mg/kg). Likely Vymazal et al. [60] provide substrate for periphyton and bacteria, take up nutrients and in carbon-limited systems provide carbon for denitrification during biomass decomposition. It has been reported that treatment performance of planted FWS CWs is superior to unvegetated lagoons. However, treatment performance of FWS CWs could be affected by plant species used. The literature survey of 643 FWS CWs from 43 countries recorded 150 plant species and revealed that the most commonly used macrophyte genera were Typha, Scirpus (Schoenoplectus observed that the Mn^{2+} concentration in the sediment of hybrid CW system was 507 mg/kg. These results are comparable with the average Mn^{2+} concen-

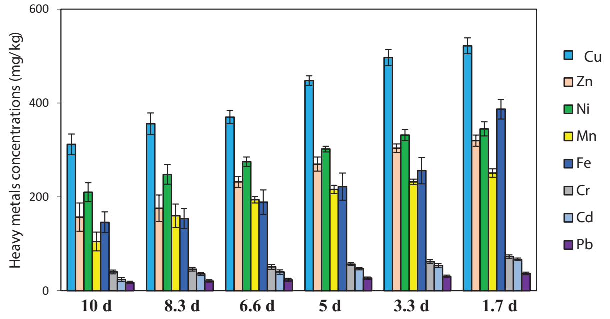

Fig. 7. Retained heavy metals concentrations in sand and gravel beds of BSCW.

tration of 434 mg/kg reported by Vymazal and Krása [61]. A higher Fe^{3+} concentration 8659 mg/kg in sediments of hybrid CW was reported by Vymazal et al. [62]. Eckhardt et al. [63] reported lower Fe^{3+}concentrations of 500–2700 mg/kg for the CW treating landfill leachate. Chagué-Goff and Rosen [64] found the Fe^{3+} concentration of 250,000 mg/kg in the sediments of a natural wet land receiving wastewater for 35 years. Pb^{2+}, Cd^{2+}, and Cr^{3+} accumulation rates were relatively lower most likely due to the low concentrations in the influent.

4. Conclusions

Non-vegetated baffled submerged constructed wetland (BSCW) system is appropriate and economically feasible technology for the treatment of hyper-saline hazardous landfill leachate (HHLL). However, the COD fractions and nitrification efficiency is largely deteriorated by reducing the HRT from 10 to 1.7 d. The BSCW reduced the toxicity (EC_{50}) of the HHLL from 2.5 to 1.25 which accounted for 50% at an HRT of 10 d. The anaerobic condition prevailed in the bottom layers of packing media in non-vegetated BSCW was presumably enhanced the activity of SRB, which reduced the sulfur compounds (48 mg SO_4/L) present in HHLL to sulfide (38 mg/L). The production of sulfide caused an increase in the pH value from 8.16 ± 0.14 to 9.1 ± 0.16 due to the consumption of proton in the sulfate ions. The sulfide was likely to react with the dissolved forms of heavy metals forming thermodynamically stable metal sulfide complexes which could be precipitated on gravel and sand beds. The accumulation of heavy metals in the sediment was for 522 ± 17 mg/kg Cu^{2+} followed by 387 ± 21 mg/kg for Fe^{3+}, 345 ± 15 mg/kg for Ni^{2+}, 345 ± 15 mg/kg for Zn^{2+} and 251 ± 9 mg/kg for Mn^{2+}.

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